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Sudarshan, Tangali. S

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University of South Carolina
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Columbia SC 29208

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Research is conducted to investigate the epitaxial growth of thick films using halogenated precursors: chlorine-based dichlorosilane (DCS) and fluorine-based tetrafluorosilane (TFS). TFS (SiF4) has been utilized for the first time to completely eliminate Si droplet formation and suppress parasitic deposition, thus enabling high quality SiC growth. Ni/4H-SiC Schottky diodes fabricated on TFS-grown epilayers show superior performance with high barrier heights and low ideality factors.

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Development of High Quality 4H-SiC Thick Epitaxy for Reliable High Power Electronics Using Halogenated Precursors

Final Technical Report: Award No.: N00014-10-1-0530 August 2, 2016

Office of Naval Research
875 North Randolph street
Arlington, VA 22203-1995
Program Manager: Dr. Harold Scott Coombe

Submitted by:
University of South Carolina
Department of Electrical Engineering
PI: Dr. Tangali S. Sudarshan

I. Introduction

Development of robust semiconductor devices with high energy efficiency and reliability is a key objective towards 'Energy Conversion and Power Management' for naval system applications. The goal of this research program is to contribute towards the reaching of the above objective by creating the fundamental knowledge needed for the development of novel approaches to synthesize high quality, thick SiC epitaxial layers (>100μm) for reliable high voltage (≥10kV) / high power (>100kW) electronics for navy ship applications. This program focuses on (a) developing innovative solutions to the current main limitation in SiC homoepitaxy - reduction/elimination of device-killing defects; (b) gaining understanding of the chemical vapor deposition processes in SiC epitaxy - specifically related to precursor gas decomposition dynamics and subsequent parasitic deposition of Si, C and SiC on the gas injector tube walls: these factors significantly influence the epilayer quality, and hence, the properties of devices fabricated on the SiC epitaxial platform; and (c) achieving both high growth rate and high quality epitaxial films in a cost-effective manner.

II. Abstract

In this program, research is conducted to investigate the epitaxial growth of thick films using halogenated precursors: chlorine-based dichlorosilane (DCS) and fluorine-based tetrafluorosilane (TFS). Growth using DCS is extensively studied, showing high growth rate (>25μm/h), excellent doping control (n+, n-, SI, p-), good epilayer morphology (RMS<2nm for 4° SiC) and low defect densities (BPD, IGSF densities 0~5.6cm^{-2}). Extensive study of dichlorosilane provides evidence that even chlorosilane gases are not the best solution to eliminate Si droplet formation and suppress parasitic deposition, which subsequently degrades crystal quality. The understanding gained from this research led to the first use of fluorinated silicon precursor with much stronger bonds to grow SiC epitaxy. Tetrafluorosilane (TFS, SiF_4)

has been utilized for the first time to completely eliminate Si droplet formation and suppress parasitic deposition by 80%. The ability of TFS to suppress particulates enables long duration, high quality thick epitaxy in the cleanest reactor environment. Epitaxial film growth rate, the influence of C/Si ratio of the precursor gases on doping concentration and crystal quality, growth process conditions, etc., have been being investigated.

High quality, thick epitaxy (120 μm) was demonstrated on 8° substrate at a growth rate of 30μm/h using TFS. Excellent control of the uniformities of doping level and morphology makes TFS especially suitable for large wafer and multi-wafer CVD growth to achieve SiC devices with excellent performance uniformity. In terms of epilayer quality including morphology, roughness, crystallinity, polytype inclusion, BPD density, etc., epigrowth using TFS is found to be superior to the growth using DCS or silane gases. Defect free epilayer growth (~0 BPD density) was achieved by a two-step epilayer growth by growing a buffer layer epi- eutectic etch- regrowth process using DCS precursor.

High quality on- axis epilayers were grown using TFS at low flow rates (5 sccm) with increased step flow growth at high C/Si ratio offering the potential for defect free epilayers, a significant breakthrough SiC technology.

Ni/4H-SiC Schottky diodes fabricated on DCS-grown and TFS-grown epilayers show similar barrier heights (>1.6eV) and ideality factors (<1.1). The tightest distribution of Schottky parameters is reported for Ni/SiC Schottky system fabricated on TFS-grown epilayer.

III. Technical Objectives

(1) In order to produce robust and high performance devices that are fabricated on the SiC epitaxy platform, it is essential that malignant defects, such as in-grown stacking faults (IGSFs) and basal plane dislocations (BPDs), be eliminated or reduced to a specific density, since those defects are known to be detrimental to the performance of high power SiC bipolar devices for power electronic building blocks in a Navy ship system. The main objective of this research is to develop a simple, efficient, and practical technique/method of synthesizing high quality thick epitaxial films grown at high growth rates desired for both DoD and commercial applications.

(2) The currently used SiC-Chemical Vapor Deposition (CVD) epitaxial growth process using traditional CVD gas precursors is not suitable for achieving the objective (1) above. Therefore, an objective of this research is to conduct in-depth research on the development of new CVD concepts based on *new gas precursors* to control the growth process and to achieve the desired high quality thick SiC epilayers.

(3) High voltage devices capable of blocking ≥25kV require high quality (low defect density) SiC epilayers with film thicknesses exceeding 150μm. One of the significant challenges in obtaining such high quality thick SiC epitaxial films using conventional silicon precursor gases is to restrict/eliminate Si gas phase nucleation and parasitic deposition and related

particulate downfall, which is specifically severe at the high growth rate or long duration growths. Chlorinated silanes with higher Si-Cl bond strength are successfully used in suppressing Si droplet formation in *silicon* epitaxy; however may not be the best option for high temperature *silicon carbide* epitaxy since the Si-Cl bond is not the strongest among silicon halogen gases. The goal of this research is to maximize Si droplet suppression using a fluorinated silicon precursor for high temperature silicon carbide epitaxy in order to achieve high quality, thick SiC homoepitaxy for next generation power applications.

(4) Liquid and solid particles formed in the reactor at different gas decomposition conditions affect crystal growth not only by reducing the growth rate but also generating defects and degrading surface morphology. Here, the objective is to undertake a systematic study to understand the generation methods and the influence of these in-grown particles on crystal quality.

(5) Even though the inlet C/Si ratio is kept fixed, the C/Si ratio at the growth surface varies depending on the different gas decomposition conditions (which is a function of temperature, pressure etc.). The C/Si ratio at the epi growth surface can be defined as the effective C/Si ratio and it depends on the relative losses of carbon and silicon in the growth chamber. Hence, the objectives are to study (a) Si-depletion in the reactor due to Si gas phase nucleation and parasitic deposition, (b) C-depletion due to the pyrolysis of propane, and (c) C-gas phase nucleation due to formation of heavier C-rich polymers in the gas. A detailed study is carried out in search of C-depletion in the reactor and the effect of C-depletion on epitaxial growth.

(6) Development of low doped ($<2x10^{14}$ / cm^3) and semi insulating ($>10^5$ohm cm) epitaxial films grown at high growth rates (>25μm/hr) to produce thick epitaxial films (>100μm) on 8° and <4° off cut SiC substrates that are essential to fabricate high voltage power devices (>5kV) for navy applications.

IV. Technical Approach

(1) The approaches employed for the growth of thick epitaxial layers at high growth rates include (a) the use of a chlorine-containing gas precursor DCS. The major advantage of using DCS as a precursor is reduced gas phase nucleation or aerosol formation, which in turn increases the growth rate and improves surface morphology. (b) Optimization of the reactor design and growth parameters using modeling software.

(2) Reactor furniture is identified to be one of the main causes for the formation of defects, such as particles, IGSFs, growth pits, etc., in SiC epilayers. Different furniture materials are used to determine their influence on the growth rate, doping, morphology, and quality (generation of additional defects). Two CVD reactor types, a chimney reactor and an inverted chimney reactor, are assembled; the latter is more flexible in varying the temperature zone for precursor decomposition and in the use of different precursors. These approaches enable the research to be not limited to a single reactor geometry, and will be very helpful in exploring

SiC-CVD processes and thus find an optimized condition for the production of high quality thick SiC epitaxial layers.

(3) A novel chemical treatment method of the SiC substrate, in a controlled manner, is established based on KOH-NaOH-MgO eutectic etching/pretreatment. This method is superior to the conventional KOH etch method. The mild etching/treatment of the SiC substrate leads to elimination/reduction of BPDs propagating into the grown epilayer, while maintaining good surface morphology. This approach has high potential to be practically applied in routine pretreatment of SiC substrates in the SiC-CVD process. This approach is also combined with suitable in-situ H_2 pretreatment to achieve the most desired outcome (to achieve 100% BPD conversion in a highly doped buffer-layer).

(4) A special technique is developed, to study precursor gas decomposition in the reactor and its influence on parasitic depositions on the reactor wall and subsequent crystal quality, by using an axially split injector tube through which the gas precursors are delivered to the growth zone.

(5) A completely new approach is taken to eliminate Si droplet formation and suppress parasitic deposition significantly compared to any conventional method applied in the past by using a fluorinated gas to achieve thick, high quality epitaxy. The highest bond strength of Si-F bond among all halogenated silanes is utilized instead of the weaker Si-Cl bond in suppressing the Si-Si bond (droplet) formation to create Si clusters.

V. Results and Discussion

1. Elimination of Si droplet and parasitic deposition using novel SiF_4 gas

High quality, thick (~100μm), low doped and low defect density SiC epitaxial films are essential for high voltage (blocking voltage >10kV), light, compact and reliable next generation power devices. One of the significant challenges in obtaining high quality thick SiC epitaxial films is to restrict/eliminate the Si gas-phase nucleation or aerosol formation during growth. The generated aerosol particles adversely influence growth by reducing the growth rate due to precursor losses, and also affect crystal quality [1], since the Si droplets are carried to the crystal growth surface. Moreover, liquid aerosol particles adhere to the various reactor parts (parasitic deposition), and contribute to their severe degradation during epitaxial growth. These parasitic depositions are generally loosely bound, and can be carried to the growth surface during growth as particulates, resulting in degradation of crystal quality by introducing defects in the growing epitaxial layers [2, 3]. The aforesaid condition is specifically severe at higher precursor gas flow rates or in long duration growth required to achieve high quality thick epitaxy since parasitic deposition and related particulate formation are also increased at these growth conditions. At this parasitic deposition enhanced condition, the cost of growth is also expected to increase due to frequent replacement of degraded reactor parts.

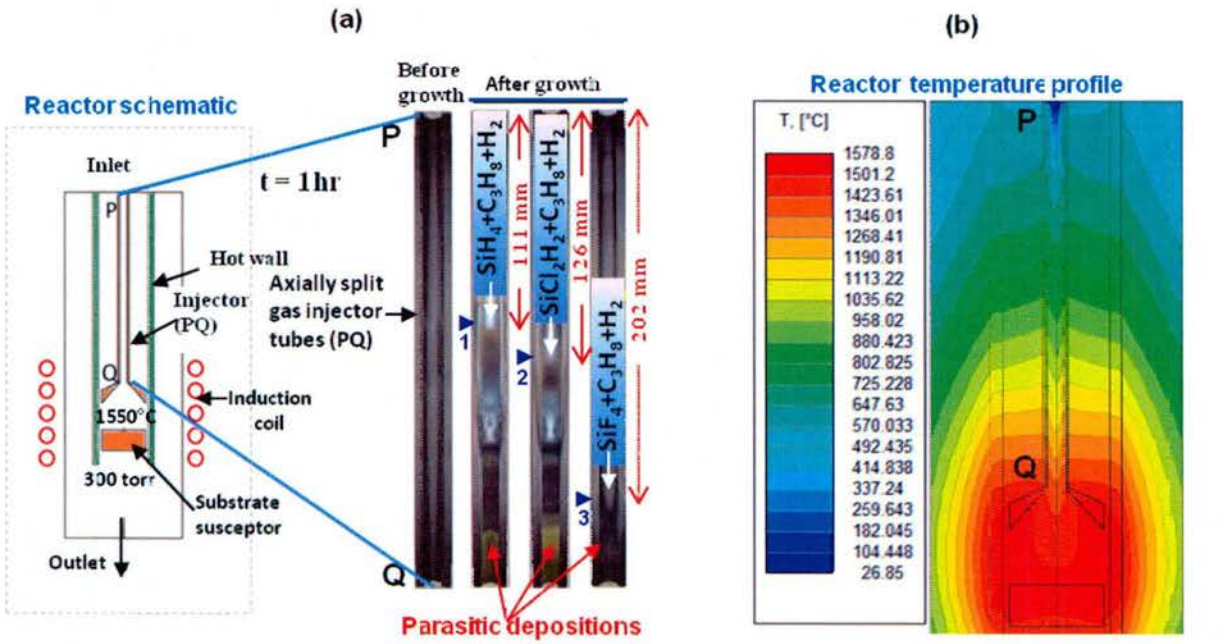
Silicon droplet formation and reactor degradation (parasitic deposition and particulates) can be improved compared to silane using a chlorinated silane [4], as Si creates bonds stronger with Cl than with another Si [5], thus reducing the possibility of Si cluster formation.

The use of chlorinated precursors represents an improvement over the use of conventional silane. Yet, many challenges still remain for commercial production of thick SiC epitaxial films. Increased visible morphological defects due to particulate downfall on the substrate caused by parasitic deposition is reported to be a limiting issue in achieving thick epitaxial layers [6]. Particulate related defects were also pointed out to be reason for low yield of device quality material in thick epilayers grown by hot wall CVD [7]. Hence, increased parasitic deposition related particulates are a crucial limiting factor preventing thick epilayers for commercial production.

A split gas delivery tube system (gas injector) was used to visualize parasitic deposition in the tube [3]. This design is an effective tool to identify the location where the gases start decomposing in the injector tube by the observation of parasitic deposition. In this scheme, the gas delivery tube was axially split into two halves, which was then reassembled for growth. The scheme is shown in Fig. 1a where the split part of the gas delivery tube can be seen as PQ in the CVD reactor. The split halves were assembled together to form a complete tube before growth, and was separated again after the growth for post examination. The inside image of one half of the split tube before and after growth is shown in Fig. 1a. Here it can be seen that the tube is clean before the growth. However, after growth, parasitic deposition, composed of different Si and C compounds, can be clearly seen. The location where gas decomposition begins prior to reaching the growth surface is estimated from the locations of parasitic deposition regions in the tubes. This technique is proven to be beneficial especially for comparing the extent of parasitic deposition for different gas chemistries in a CVD reactor.

The Si-F bond is the strongest among all halogenated silanes (Si-F: 565kJ/mol; Si-Cl; 381kJ/mol; Si-Br: 309 kJ/mol and Si-I: 234 kJ/mol) [8, 9]. The dissociation bonding energy of any halogenated Si-X bond is higher than that of the Si-Si bond (222 kJ/mol) [9]. Hence Si forms a stronger bond with the halogen than with Si itself, suppressing Si cluster formation.

The possibility of Si gas phase nucleation due to increased partial pressure of elemental Si, decomposed from DCS (SiH_2Cl_2) when the major mediating species for growth is changed from gaseous $SiCl_2$ to elemental Si, is discussed in [4]. The Si-Cl bonds in chlorinated silanes may completely dissociate at the high SiC growth temperatures and form elemental Si, leading to super saturation and formation of liquid silicon droplets at higher flow rates. This condition, rich with elemental Si, reduces the growth rate due to gas phase nucleation, leading to growth rate values not significantly higher than those using silane [4].



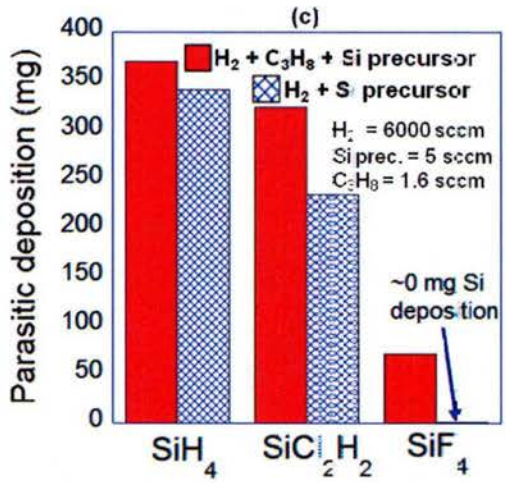


Figure 1 (a) Reactor geometry showing the position of the split gas-injector tube (left). Split tube before growth and parasitic depositions after growth are shown for different silicon precursor gases with propane and hydrogen. The locations from where the parasitic deposition starts are marked as 1, 2 and 3 for silane, DCS and SiF_4 respectively. (b) Temperature profile in the reactor obtained using a simulation tool is shown. (c) Bar graph showing the masses of parasitic depositions on gas injector walls using silane, DCS and SiF_4 precursor gases *with* and *without* propane addition. An ~80% reduction of parasitic depositions for SiF_4 *with propane* and a ~100% reduction *without propane* was found. (T= 1550°C, P= 300 torr, H_2 flow rate = 6 slm, propane flow rate = 1.6 sccm, Si precursor flow rates = 5 sccm and duration = 1hr).

Thus, similar to silane, even chlorinated silanes have a threshold (though higher than silane), above which increasing the precursor flow initiates Si supersaturation and droplet formation, limiting the maximum achievable growth rate. This threshold for increasing precursor flow can be extended further than with chlorinated silanes (without Si gas phase nucleation) using a precursor with a stronger Si-X bond. This leaves fluorinated silanes (SiH_xF_y; x= 0, 1, 2, 3 and y =4-x) as the remaining choices.

Silicon tetrafluoride (TFS) is a very stable gas. TFS molecules do not react with hydrogen below 2000°C, whereas chlorinated silanes are reduced by hydrogen at 1000°C or below [10]. This implies that TFS does not thermally decompose at typical SiC growth temperatures. Hence, the CVD growth of SiC using TFS is assumed to be mainly mediated by un-decomposed TFS molecules. This unique property of TFS to remain un-decomposed in the SiC growth environment effectively eliminates Si droplet formation, reduce parasitic deposition, prevents Si precursor losses, and ensures the cleanest possible particulate-free growth condition compared to any other silicon gas precursors.

To study parasitic deposition, which also indicates how early the gas decomposes in the reactor, the split gas injector tube as described earlier is utilized. The photographs in Fig. 1a qualitatively show the degree of parasitic deposition and the approximate location where gas decomposition begins to take place in the gas delivery tube for TFS in comparison with conventional gases. In Fig. 1a, three split gas injector tubes (their location shown in the reactor geometry) are shown after the epitaxial growths with different gases using the same growth conditions. A gas mixture of a silicon precursor gas (SiH_4 / DCS/ SiF_4) *with* or *without* propane, along with hydrogen, enters the cold end of the tube, and exits the hot end towards the growing crystal. During this travel, silicon/carbon compounds deposit on the tube wall starting at ~700°C, ~950°C and ~1200°C for SiH_4, DCS and SiF_4 precursors respectively (estimated from Fig. 1b). Clearly, from Fig. 1a, for similar growth conditions in the reactor, SiF_4 initiates parasitic deposition later in the gas stream (202mm from inlet) producing the least amount of parasitic deposition compared to SiH_4 (111mm) and DCS (126mm) due to much higher Si-F bond energy (565 kJ/mol) of SiF_4. The measured weight of these depositions from the weight difference of the injector tube measured before and after growth is shown in a bar graph in Fig.1c.

For TFS, approximately ~0mg of Si deposition (compared to 341mg for SiH_4 and 235mg for DCS) was measured for the case *without propane* indicating *Si deposition-free* condition in the reactor essential for high quality growth in a clean reactor environment (implying minimum Si pyrolysis and minimum gas phase nucleation). On the other hand, *with propane* addition, only 71mg of parasitic deposition took place on the gas injector tube observed for SiF_4 compared to 370mg and 323mg respectively for SiH_4 and DCS (an ~80% suppression of parasitic deposition using SiF_4; no significant difference was observed for DCS and SiH_4 gases). This significant suppression of parasitic deposition obtained using SiF_4 is an important consideration for achieving high quality thick epitaxy by long duration growths [6]. Suppression of parasitic deposition using SiF_4 does not only improve the crystal quality by minimizing parasitic particles originating from the reactor parts but also increases the re-usability of the reactor parts, which is an important factor to reduce the growth cost.

A large number of particulate related defects (Fig. 2) were observed for the growth using SiH_4 at 5sccm for one hour growth at a growth rate of ~7μm/hr. These large particles were directly related to the degradation of the reactor parts due to severe parasitic deposition and their consequent particle downfall on the growth surface. Long duration growth with good

morphology was not possible in this case. The density of particle related defects is shown in Table 1. Growth using DCS exhibited somewhat lower density of particles (due to lower parasitic deposition). Long run growths with good quality epilayers were still not possible even at this growth condition due to these particles. On the other hand SiF_4 suppressed parasitic deposition and gas-phase nucleation significantly and a much higher growth rate (30μm/hr) was achieved by increasing the mass transport to 10sccm. In this cleaner growth environment achieved using SiF_4, long duration growth (4 hours) with good quality epitaxy was possible and films up to 120μm thicknesses were grown at a growth rate of 30μm/h. A comparison of particulates generated during growth using three different Si precursors is shown in Table 1. Large particles on the epitaxial layer, mostly generated from loosely bound particles formed due to parasitic deposition in the gas delivery pathway were eliminated using SiF_4 gas by suppressing parasitic deposition as described earlier.

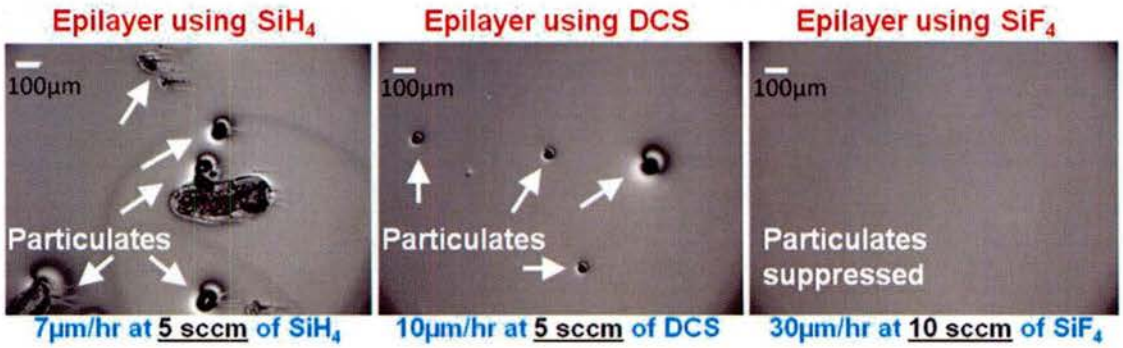


Figure 2 Particles on epilayer surface grown using various gas precursors at similar growth condition. No large particle related defects are observed for the epilayer grown using SiF_4 even at higher flow rates. (T= 1550°C, P= 300 torr, H_2 flow rate = 6 slm and duration = 1hr).

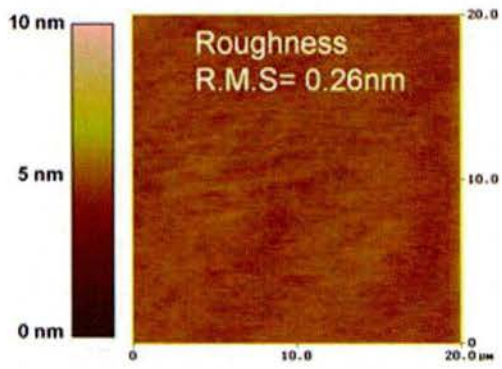


Figure 3 AFM image of a 60μm thick epilayer with excellent surface morphology grown using SiF_4.

Table 1. Comparison of epilayer quality using various precursors for (T= 1550°C, P= 300 torr, H_2 flow rate = 6 slm, C/Si =~1 and growth duration = 1hr; substrate $E_2(TO)/E_1(TO)$ or 4H/3C peak ratio = ~32, substrate doping = ~$1x10^{19}$-N-type and substrate XRD FWHM = ~20 arcsec).

Si precursor	Si gas flow rate[a] sccm	Growth rate (μm/hr)	Raman E_2 to E_1 (4H/3C) peak ratio	Doping (cm^{-3})	Surface roughness RMS[b] (nm)	XRD FWHM	Particle density 100-400μm (cm^{-2})	Particle density 30-100μm (cm^{-2})	Particle density 10-30μm (cm^{-2})	Pit density 1-3μm (cm^{-2})
SiH_4	5	7	~30	$1x10^{17}$ p	~0.5nm	~20	20	~50	~200	~$3x10^5$
DCS	5	10	~50	$5x10^{16}$ p	~0.4nm	~12	0	~45	~100	~$2x10^3$
SiF_4	10	30	~60	$1x10^{15}$ n	~0.3nm	~7.5	0	0	~5	~50

[a] epilayer surface significantly degrades with particulates at these flow rates (5 sccm) for silane and DCS. However, growth is improved due to suppression of particulate using SiF_4 even for higher flow rates (10 sccm). Fig. 2. shows the growth surfaces at these flow rates.

[b] excluding the regions with particulates in the epilayers

For SiF_4, a lower density (~ 5 cm^{-2}) of smaller sized particles (10μm-30μm) compared to silane and DCS mediated growths were observed (Table 1). Also, pits of 1μm -3μm size were significantly reduced using SiF_4 compared to silane and DCS (Table 1). We believe that these morphological defects were not growth related and mostly appeared because of downfall of particles during the loading of substrate in the reactor (located in a non-cleanroom environment). To confirm particle downfall during sample loading, the sample was loaded in the reactor, evacuated, and kept for 12 hours typical to reach high vacuum. The substrates were then unloaded without growth and particles were indeed observed on the surface by Nomarski microscope.

Morphologically, a very smooth surface (RMS roughness ~0.3nm) was observed for a ~60μm thick epilayer grown at 30μm/hr for 2 hours using SiF_4 (Fig. 3). The surface roughness does not increase much for thicker (~120μm grown over 4 hours) epilayers (RMS roughness ~0.5nm vs. ~0.3nm) using SiF_4.

In summary, the highest Si-halogen (Si-F) bond strength (565 kJ/mol) in SiF_4 among all silicon-halogen gases was utilized to create the best condition for Si-droplet or particle free environment in a hot wall CVD reactor compared to silane and chlorosilane gases. Using this fluorinated gas, parasitic deposition in the reactor and particulates in the grown epilayers are significantly reduced compared to conventional silane and dichlorosilane gases. Growth in a Si particle suppressed condition enables increasing the growth rate from 10 μm/hr to 30 μm/hr by increasing the mass flow rate with significant suppression of particulate induced defects in the epilayers compared to growths using silane and dichlorosilane gases. Reduction of silicon droplets and parasitic deposition in the reactor enabled long duration growth for high quality thicker homoepitaxial films (>100μm) with smooth surface morphology (r.m.s. roughness ~0.5nm) essential for high voltage devices in efficient next generation power electronics.

2. Reduction/elimination of basal plane dislocations (BPDs) in epitaxial growth on 4° off-axis 4H-SiC.

(1) Regular growth on untreated substrates

First, epitaxial growth on untreated 4° off-axis 4H-SiC substrates is investigated at various epilayer thicknesses. The BPD density and the conversion rate are plotted in Figure 4. It is found that the BPD density on the epilayer surface decreases with increasing epilayer thickness, which indicates that the propagating BPDs are converted during the epitaxial growth. This trend is also observed by another group using the ultraviolet photoluminescence(UVPL) characterization [11, 12]. Figure 4 shows that ~99.0% of the BPDs on the substrate surface are converted to TEDs in the vicinity of epilayer/substrate interface (within 1.5 μm epilayer thickness); the rest ~1.0% BPDs propagate into the epilayer and are converted to TEDs throughout the epilayer growth, completing the conversion within ~20 μm of the epilayer thickness.

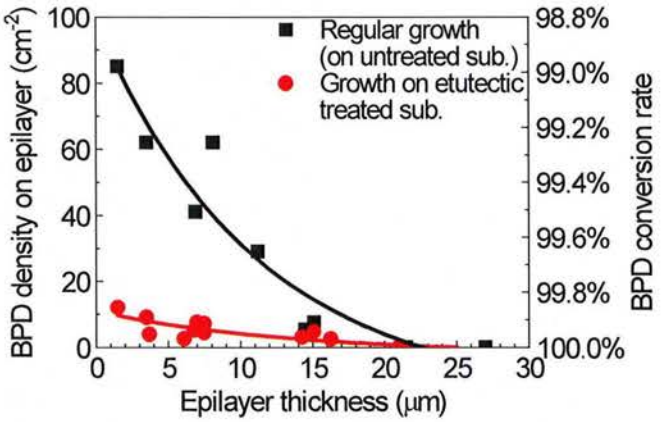


Figure 4. BPD density and conversion rate in regular growth on untreated substrates. The average BPD density on substrate is 8.4×10^3 cm^{-2}.

It is reported [13] that the buried BPDs in highly doped buffer layers can still be converted to Shockley stacking faults (SFs) under current stress; furthermore, these SFs will extend into the drift layers and degrade device performance. The deeper the depth from the epilayer surface that the BPDs are buried, the higher the current density that is required to convert them to SFs. Therefore, the buried BPDs in epilayer will still have the risk of degrading device performance. Considering this, converting BPDs to TEDs close to the epilayer/substrate interface is important in order to improve the reliability of SiC high power devices.

(2) Growth-etch-regrowth

In order to achieve 100% BPD conversion near the interface, a 1.5 μm buffer-layer was grown and then treated for 2 min in the optimal eutectic (Table 2). The main epilayer was grown on the treated buffer-layer. Results of samples 13-15 show that zero-BPD is always achieved on the main epilayer even on a 1.5 μm thick main epilayer (sample 13). Since in regular growth on the untreated substrates, ~99.0% substrate BPDs are converted to TEDs within 1.5 μm epilayer (shown in Figure 4), by means of the "growth-etch-regrowth" process, the rest of the BPDs are

all converted near the main epilayer/buffer-layer interface, instead of propagating and being converted throughout the epilayer.

Table 2. BPD density on epilayers from "growth-etch-regrowth" process

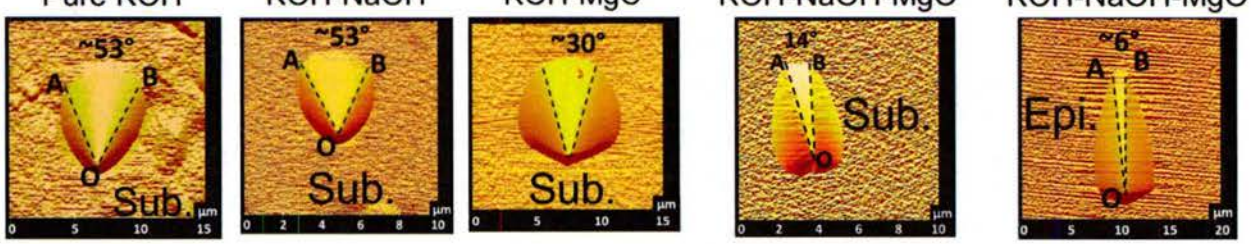
Sample No.	Buffer layer pretreatment duration in eutectic	Main epilayer Thickness (μm)	BPD density on epilayer (cm^{-2})
13	2 min	1.5	0
14	2 min	3.5	0
15	2 min	6.5	0

In summary, a practical method has been developed to pretreat 4° SiC substrates to convert 100% of the substrate BPDs near the epilayer/substrate interface. This method a "growth-etch-regrowth" process that can achieve zero-BPD even on a 1.5 μm thick main epilayer. On 4° substrates, the small angle of the sector opening of a BPD etch pit within which lateral growth dominates over step-flow growth is believed to be the reason for the very high BPD conversion rates achieved.

3. Study of the mechanism of BPD conversion/elimination

Our results show that in epitaxial growth of SiC on KOH-NaOH-MgO eutectic etched substrates, BPD to TED conversion ratio is significantly enhanced at the epilayer/substrate interface [14-16]. In this section, the BPD etch pit profiles are studied in different etchants: pure KOH, KOH-NaOH eutectic, KOH-MgO mixture, and KOH-NaOH-MgO mixture.

BPD conversion in epitaxial growth on etched substrates is explained by enhancing lateral growth to pinch off the step-flow growth in the sector plane of a BPD etch pit [17]. The open angle of the sector plane is directly related to the efficiency of pinching off of the step-flow growth. A narrow BPD etch pit, i.e., smaller open angle of the sector plane, will lead to an easier BPD to TED conversion [16]. **Figure 5** shows the shape of BPD etch pit generated on 4° SiC surface using different KOH-related etchants.



(a) (b) (c) (d) (e)

Figure 5. AFM images of BPD etch pits generated on 4° SiC surface by different KOH-related etchants.

The etch pits formed on 4° SiC substrates with molten pure KOH and KOH-NaOH eutectic are shown in **Figure 5a and 5b**, respectively. It is found that the open angle (∠AOB) of the substrate BPD etch pit is about 53°. Using KOH-MgO mixture, the BPD open angle is ~30° (**Figure 5c**). In our experiments on 4° SiC epigrowth, these three etchants do not show any enhancement of BPD conversion compared with growth on untreated substrates. Using our developed KOH-NaOH-MgO eutectic mixture, the open angle (∠AOB) of the substrate BPD etch pit is about 14° (**Figure 5d**) and a significant enhancement of BPD conversion ratio was found (from ~99.0% conversion ratio in growth on untreated substrate to ~99.9% conversion ratio in growth on etched substrate) [16]. Furthermore, etch of SiC n^- buffer epilayer using our developed KOH-NaOH-MgO eutectic mixture generates the smallest open angle (∠AOB=6° in **Figure 5e**) in BPD etch pits, thus a 100% BPD conversion ratio.

Using the molten KOH-related etchant, the etch rate on the SiC (0001) Si face is very low in the stress-free area [19, 20], but it is much higher around the strained area where a dislocation intersects the surface; consequently, the surface is etched along the dislocation line direction. This is the reason why a molten KOH-related etchant is conventionally used to reveal defects on a SiC (0001) Si face [21, 22]. Generation of a narrow BPD etch pit (**Figure 11**) is caused by the high degree of anisotropic etching, i.e., higher etch rates in the <11-20> directions ($ER_{<11\text{-}20>}$) versus in the <1-100> directions ($ER_{<1\text{-}100>}$). Therefore, using the modified KOH-NaOH-MgO eutectic etching, including very mild etching (e.g., 3min), the anisotropic etching behavior is significantly enhanced; consequently the BPD conversion rate is enhanced.

4. Highly n-type doped SiC epilayers grown using DCS precursor

Highly n-type (up to 1e18 cm^{-3}) doped SiC epilayers have been successfully achieved in our HTCVD furnace using DCS precursor. The effects of C/Si ratio and nitrogen flow rate on epilayer quality, including the surface morphology, BPD conversion and defect generation, were studied systematically.

Figure 6 shows the growth rate at various C/Si ratios (with constant DCS flow rate of 4.2sccm). The growth rate increases with C/Si ratio for C/Si<1, and then reaches saturation for C/Si>1. This indicates a C supply limited growth at C/Si<1 and Si supply limited growth at C/Si>1. This trend is quite common as observed in SiC growth using silane. Addition of N_2 does not show detectable influence on the growth rates.

The unintentional doping concentration at various C/Si ratios is shown in Fig. 7. This doping dependence behavior agrees with the "site competition" theory. Semi-insulating (SI) epilayers can be achieved for C/Si:1.4–1.7. In the case of intentional doping, the n-type doping concentration increases with the N_2 flow rate as shown in Fig. 8. Theoretically, the desired high n-type doping concentration could be achieved at any C/Si ratio with addition of N_2 at a suitable flow rate, therefore, it is necessary to determine at which condition (C/Si ratio) the epilayers have the highest quality in terms of morphology, defects, etc.

The RMS surface roughness was measured by AFM (Fig. 9) for the unintentionally doped epilayers. The RMS value decreases significantly with increasing C/Si ratio from 0.4 to 1.3, and the value has no significant change for C/Si>1.3. Uniform step-bunching is observed on these 4° epilayers with the macro-step height 6–8 nm (Fig. 10). Addition of N_2 only causes slight increase in RMS values (by ~10% while the doping concentration increases to 10^{16}–10^{18} cm^{-3}). This indicates that in the epitaxial growth using DCS, the highly n-type doped epilayers are preferable to be achieved at a higher C/Si ratio (>=1.3) by adding N_2.

The morphological defects are different for the epilayers grown at different C/Si ratios. The carrot defects and large growth pits are observed on the epilayers grown for C/Si: 0.4–0.7. It is believed that the generation of these defects is related to the Si-droplet formation from the excessive Si-containing species at too low values of the C/Si ratio. The inverted pyrimids and triangular defects are observed on the epilayers grown at C/Si~1.1. For C/Si: 1.3–2.6, the epilayers are almost free of the above morphological defects, but occasionally have some shallow growth pits in the density <20cm^{-2}. At C/Si>3.0, very large triangular defects identified as 3C inclusion are observed.

The basal plane dislocation (BPD) density on the epilayer reduces with increasing C/Si ratio for C/Si: 0.4–1.1 (Fig. 11), and then does not change for C/Si: 1.1–2.6. The lowest BPD density of 0–5.6 cm^{-2} has been achieved for a wide C/Si range. The BPD density on the substrates is ~5000 cm^{-2}. This indicates that the BPD to TED conversion ratios are greater than 99.8% for C/Si: 1.1–2.6 in this study. The in-grown stacking fault (IGSF) density of 0–5.6cm^{-2} was achieved for C/Si:1.1–1.8. Significant increase of IGSF density (~10^2 cm^{-2}) is observed for low (<=0.7) or high (>=2.2) C/Si ratios. This may be attributed to the 2D nucleation from the excessive Si or C containing species on the growing surface.

The above studies indicate that in epigrowth using DCS gas, high quality highly N doped SiC epilayers should be fabricated at C/Si ratio=1.3~1.8 with addition of sufficient amount of N_2. Epilayer quality including defects on the epilayer is mainly influenced by C/Si ratio. Addition of N_2 does not show noticeable effects on the defects, but may slightly degrade the surface morphology.

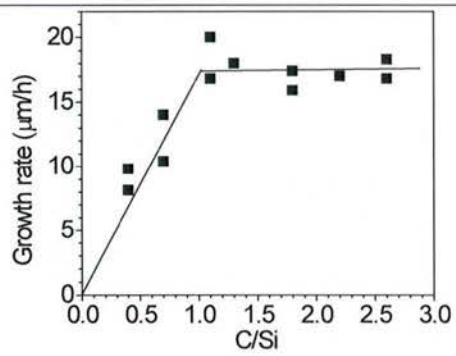


Figure 6. Growth rate vs. C/Si ratio (with constant DCS flow rate).

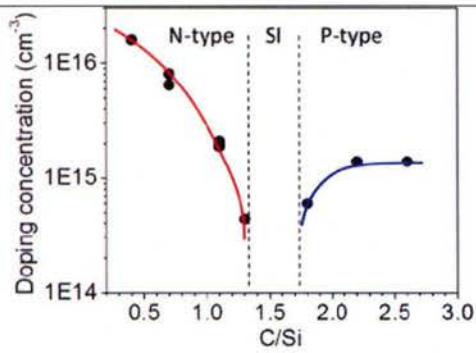


Figure 7. Doping concentration vs. C/Si ratio.

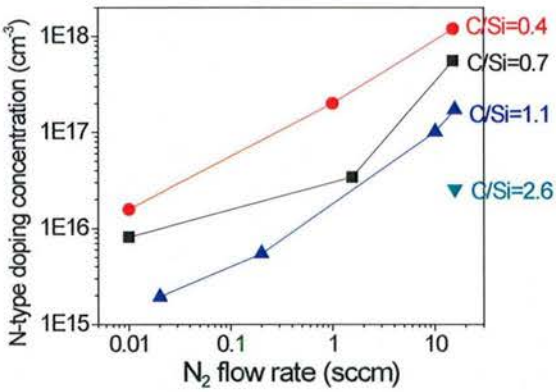


Figure 8. Doping concentration vs. N_2 gas flow rate at various C/Si ratios.

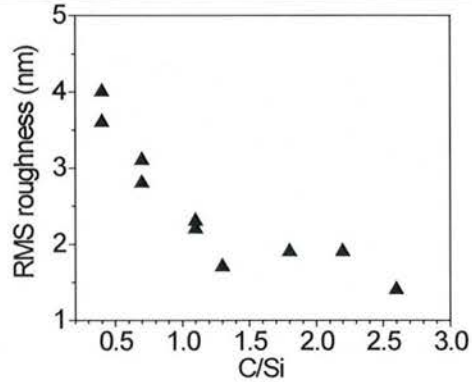


Figure 9. RMS surface roughness at various C/Si ratios.

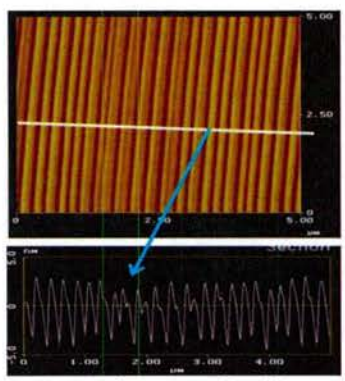


Figure 10. AFM image of epilayer grown at C/Si=1.3, showing step-bunching.

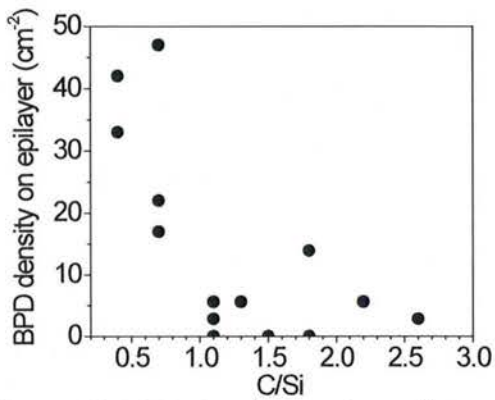


Figure 11. BPD density on the epilayer at various C/Si ratios.

5. Good Quality Epitaxial Growth on Larger area Substrates

Highly n-type doped (up to 1e18 cm^{-3}) SiC epilayers have been successfully achieved in our HTCVD furnace using DCS precursor. The effects of C/Si ratio and nitrogen flow rate on epilayer quality, including the surface morphology, BPD conversion and defect generation, were studied systematically, as reported in the previous sections for epilayers grown on 12mmx12mm SiC substrate samples. The growth of reproducible good quality epilayers were extended to 25mmx25mm SiC substrate samples. The growth process was optimized at temperature 1595^0 C, pressure 80Torr, with 1 minute unintentional H_2 etching in H_2+C_3H_8, to produce epilayers free of morphological defects such as carrots, triangular defects, and inverted pyramids. The BPD density was ~9 cm^{-2}, corresponding to a BPD conversion ratio of above 99.6% (based on the substrate BPD density of ~4000 cm-2), and the in-grown stacking fault (IGSF) density was ~6 cm-2. The growth rate was approximately 9μm/hr and the rms surface roughness, determined using AFM, was 1.9-2.5nm, with an edge-exclusion region of 3mm. These results are very promising in terms of extending the epi process, developed under this program, to commercial wafers 4"-6" in diameter, in a commercial reactor.

6. Comparative study of 4H-SiC homoepitaxial growth using TFS and DCS precursors

In SiC epitaxy different Si precursors show specific influence on the epilayers grown. For the first time comparative studies were made for epilayers grown using halogenated silicon precursors, dichlorosilane (SiH_2Cl_2, DCS) at 5.6 sccm and tetrafluorosilane (SiF_4, TFS) at 10 sccm and 5 sccm with special focus on Si gas phase nucleation, parasitic deposition and defect density. All the growths were carried in our home built vertical hotwall CVD reactor on 4° offcut 4H-SiC substrates diced to 8mmx8mm in size. Growth temperature was 1600°C and pressure was maintained at 300 Torr. Si precursor flow rates were kept constant and C precursor (C_3H_8) flow rate was varied accordingly to change the C/Si ratios with H_2 as the carrier gas in the reactor.

It was observed that epitaxial growth using TFS greatly suppresses parasitic deposition in the gas delivery system even at high flow rates. Growth using TFS shows carbon mediated growth regime, and exhibits controlled (unintentional) doping concentration of the epilayer by an order of magnitude lower than that in the growth using DCS at the same C/Si ratio. High flow rate growth of TFS exhibits non-saturating high growth rates (~31um/hr) even at high C/Si ratio of 2.0. Studies of epilayer surface morphology show that the epilayers from TFS (high flow rate) growth have a specular surface in a wide C/Si range whereas in the growth using DCS and TFS at low flow rates, the epilayer surface roughness is strongly dependent on the C/Si ratio.

As shown in fig.12, TFS and DCS growths at low flow rates show similar growth rate behavior but growths using TFS at a high flow rate show non-saturating growth rates with increasing C/Si ratio, with good surface morphology.

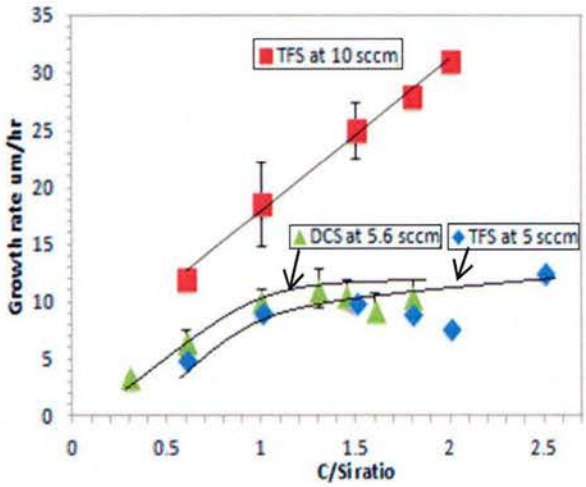


Fig.12. Growth rate vs. C/Si ratio curves for DCS (5.6 sccm) and TFS (10 sccm & 5 sccm)

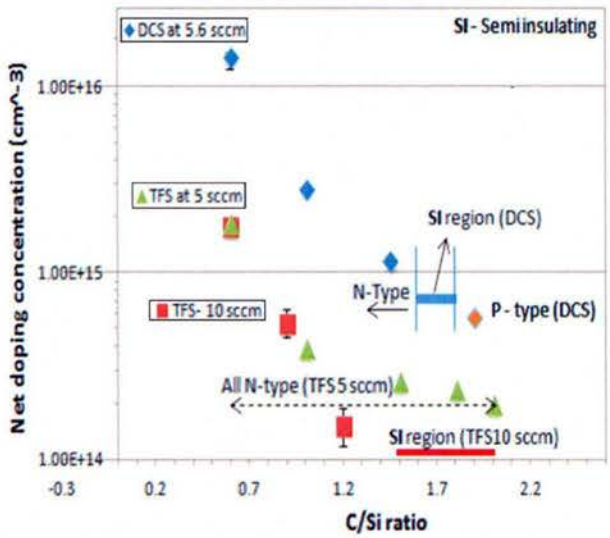


Fig.13. Net doping concentration vs. C/Si ratio curves for DCS (5.6 sccm) and TFS (10 sccm & 5 sccm)

Parasitic deposition is one of the major reasons that limits epilayer quality and is severe for high growth rate and/or long duration growth for thick epilayers. Fig. 14 shows the CVD furnace geometry and temperature distribution obtained by simulation using the *Virtual Reactor* software. Fig. 15 shows the split injector tube and bottom view of the injector cap before and after growths using DCS and TFS for the same C/Si ratio = 1.8 and Si flow rate (10 sccm). The parasitic deposition could be found as yellowish depositions on the walls. For DCS-growth, the parasitic deposition starts at ~900°C, reaches the maximum at ~1250°C on the injector tube (Fig. 15b), and then reduces on the injector cap (Fig. 15e), whereas for TFS-growth, the parasitic deposition occurs at ~1400°C mostly on the injector cap (Fig. 15f). By weighing the injector tube and cap before and after epigrowth, the overall parasitic deposition in TFS-growth is much less (50~80%) than that in DCS-growth. TFS by itself does not decompose even at a temperature of 2000°C. It is evident that the presence of hydrocarbons makes TFS or its derivative compounds decompose at a temperature below 2000°C resulting in parasitic deposition on the injector cap portion. This also suggests that the epigrowth of SiC using TFS is C mediated.

Basal plane dislocations (BPD) density was studied on selected epilayers after molten KOH etching, as shown in Table 4. Both in DCS and TFS (5 sccm) growths the BPD density is high at a low C/Si ratio of 0.6. The BPD density increases when DCS flow rate increases from 5.6 sccm (growth rate ~11.8 μm/h) to 10 sccm (growth rate ~ 28 μm/hr). However, for TFS-growth at high flow rate of 10 sccm for C/Si =1.8 (growth rate ~28 μm/h), low BPD density are preserved. It can also be inferred from Table 1 that BPD density reduces with increase in C/Si ratio and for increasing thickness of epilayers. TFS growth produced good morphology even at high C/Si ratio and increased growth rate which is advantageous for reducing the BPDs in the epilayer.

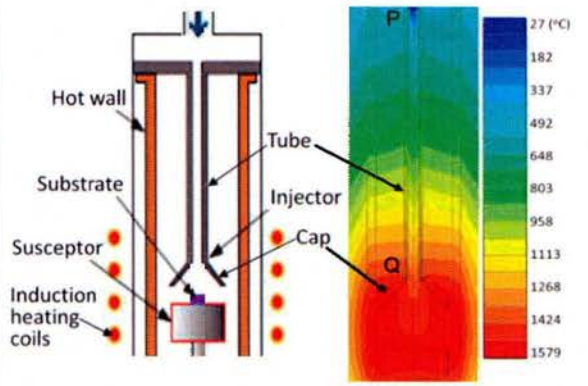


Fig.14: CVD furnace geometry and temperature distribution (simulated using *Virtual Reactor*)

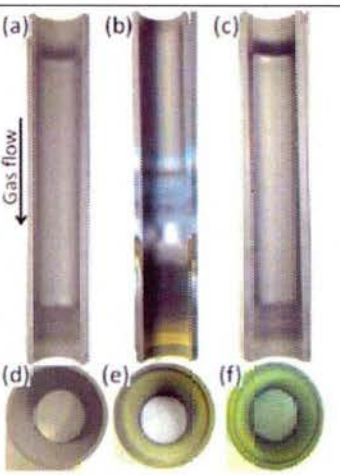


Fig.15: Deposition on injector tube (split) and Injector cap (bottom view) for 1hour growth with 10 sccm DCS or TFS. (a) and (c):before growth; (b) and (e): after DCS-growth; (c) and (f): after TFS-growth.

Table 3: Basal Plane Dislocation density on epilayers grown using DCS (5.6 sccm) or TFS (5 & 10 sccm)

Precursor	C/Si	BPD (cm^{-2})
DCS 5.6 sccm	0.6	114
DCS 5.6 sccm	1.6	6
DCS 10 sccm	1.8	19
TFS 10 sccm	0.6	14
TFS 10 sccm	1.8	6
TFS 5 sccm	0.6	202
TFS 5 sccm	1.8	42

7. High doped layer growth on buffer layer-etched epi-substrate to eliminate BPDs

A novel method to produce BPD free epilayers for fabricating high power P-i-N diodes was successfully investigated using DCS precursor. The method consisted of a two-step epilayer growth process. First, a thin n-type doped buffer epilayer was grown on SiC substrate. This epilayer was subjected to KOH-NaOH-MgO eutectic etching at controlled conditions and finally another epilayer was grown on the etched epi to achieve BPD free second buffer epilayer. One set of experiments was carried on by growing n- doping (~5E15 cm^{-3}) first buffer layer (3 to 5 um) at 1600°C, 80 Torr pressure for C/Si ratio of ~1.4. The buffer epilayer was subjected to eutectic etching. The etched epilayer was systematically studied to map the defects followed by a second buffer epilayer growth with ~5 um thickness with high n-type doping (~5E17 cm^{-3}) for the same C/Si ratio of ~1.4 at 1600°C and 80 Torr pressure. KOH etching study was performed

on the second epilayer for defect analysis and 100% BPD conversion was achieved on the second buffer epilayer. The same experiment was repeated by growing a relatively high n-type doped (~1E16 cm^{-3}) thin first buffer layer (3 to 5 um) at 1600˚C, 80 Torr pressure for C/Si ratio of ~1.4. Eutectic etching was performed on the first epilayer followed by a second buffer epilayer growth with ~5 um thickness and high n-type doping (~1E17 cm^{-3}) for the same C/Si ratio, temperature and pressure. 100% BPD conversion was obtained here also. This approach is also combined with suitable in-situ H_2 pretreatment to achieve the most desired outcome (to achieve 100% BPD conversion in a highly doped buffer-layer). These results show a reliable approach in eliminating BPDs in the epilayer growth process which aids in fabricating high quality SiC power devices.

8. 4H-SiC homo epitaxy on nearly on-axis substrates using TFS

A novel method in homoepitaxial growth of nearly on-axis (±0.5˚) 4H–SiC substrates was demonstrated with TFS as the Si precursor. High quality epilayers were obtained at low flow rates of Tetrafluorosilane used as Si precursor for different C/Si ratios. Growth temperature was 1600˚C and pressure was maintained at 300 torr. H_2 (10 slm) was used as the carrier gas. Growth time was 60 minutes. The quality of the epilayers was examined using various characterization techniques. N-type doping ranging from 10^{17} cm^{-3} to 10^{14} cm^{-3} was obtained for a C/Si ratio range of 0.6 to 2.5. The approach here is to produce BPD free epilayer using low offcut substrates by BPD to TED conversion which also reduces the boule wastage occurring in wafer slicing. We report thick epilayers for nominally on-axis substrates with a maximum of ~14 um at C/Si ratio of 2.5. All the epilayers exhibited low roughness (~1 nm). These results show excellent epilayer quality that can be used to make devices like PiN diodes and BJTs with high performance index.

Varying growth rates of epilayer were obtained by increasing the C/Si ratio by keeping the Si precursor flow constant and varying the C precursor flow during each growth. As shown in Fig.16, the growth rates gradually increase with the increase in C/Si ratio. Interestingly the growth rate showed a continuous increase even at high C/Si ratio of 2.5 with very good surface morphology. This non-saturating characteristic even at high C/Si ratios is attributed to C-mediated growth mechanism in TFS growth.

Fig.17 shows the unintentional net doping concentrations at various C/Si ratios of grown SiC epilayers measured using the mercury-probe C-V method. The curve shows doping dependence behavior similar to the "site competition" theory. As the site competition states, more N-type doping is observed for low C/Si ratio and as the C/Si ratio increases due to more C-availability, the N incorporation becomes difficult thereby reducing the net doping concentration. Epilayers reported in this work exhibit N-type net doping concentration ranging from ~10^{17} cm^{-3} to ~10^{14} cm^{-3} for a C/Si ratio of 0.6 to ratio 2.5 (Fig.13). This wide range of n-type doping values makes the epilayers useful for various device applications that require electron charge carrier transport.

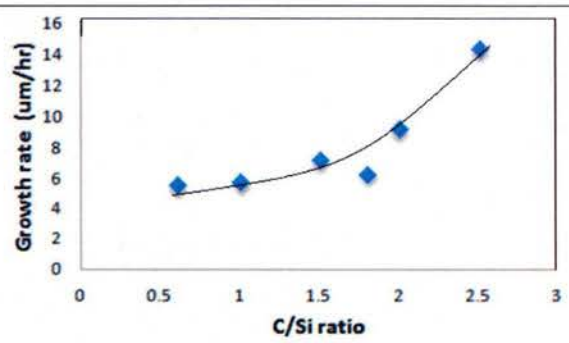


Fig.16: Growth rate vs C/Si ratio curve for nominally on-axis epilayers (trend line shown is a guide to the eyes).

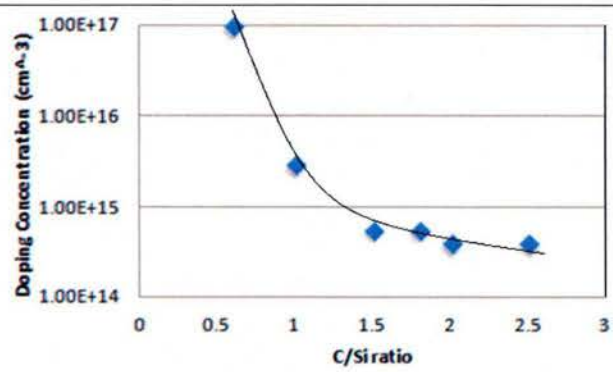
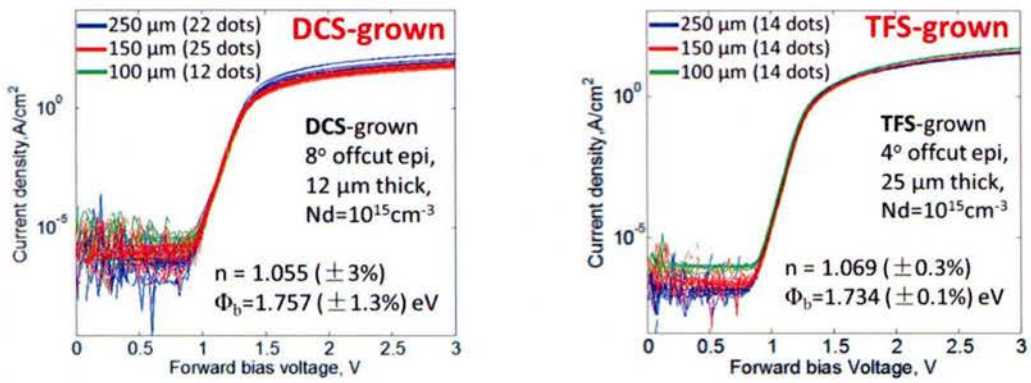


Fig.17: Net doping concentration vs C/Si ratio curve for nominally on-axis epilayer (trend line shown is a guide to the eyes).

9. Schottky diodes fabricated on epilayers grown using DCS and TFS precursors

The epilayers grown using DCS and TFS were used to fabricate test Schottky diode test structures. The surfaces of the grown epilayers were cleaned by a standard RCA procedure and were dry-oxidized at 1150°C for 4 hours. The (sacrificial) oxide layer was removed by wet etching in 1:10 HF acid solution. An Ohmic contact was formed on the backside of the highly doped substrate by depositing Nickel and rapid annealing at 1000°C in Ar ambient. The epilayer surface was patterned by standard lithography to form circular 'dots' of three different diameters — 100, 150 and 250 μm. The Schottky contact was formed by depositing Ni by e-beam evaporation at room temperature, followed by a post-lift-off rapid thermal annealing at 650°C in Ar gas. The Schottky annealing step was shown to produce highly reproducible, ideal Nickel Silicide/SiC Schottky contact [22].

Figure 18 shows a comparison between the I-V characteristics obtained from epilayers grown by DCS (a) and TFS (b). Although the average values for barrier heights and ideality factor values were similar, the standard deviations from the average values were an order of magnitude larger for the DCS-grown sample than those for the TFS grown sample. The 'tighter' distribution of the surface barrier heights for the TFS-grown epilayer infers a more uniform surface morphology and doping level over the entire epi surface. It is to be noted that the TFS data were obtained for a 4° offcut epilayer, which is expected to show a greater amount of non-uniformity in surface morphology because of the higher levels of surface step bunching as compared to an 8° offcut epilayer.



(a) (b)

Figure 18. Forward I-V characteristics for Schottky diodes fabricated on (a) an epilayer grown by DCS on 8° offcut substrate and (b) an epilayer grown by TFS on a 4° offcut substrate. The latter shows a tighter distribution of the Schottky barrier parameters among the Schottky dots. The DCS data (a) features I-V curves obtained from 22 Schottky 'dots' of 250 μm diameter, 25 of 150 μm and 12 of 100 μm. On the other hand, the TFS data (b) were obtained from 14 dots of each size.

VI. Major Accomplishments

1. Alternate Precursor CVD Growth using Dichlorosilane

Excellent doping control, from highly n-type doped (up to 1e18cm^{-3}) to semi-insulating and to low p type (~1e15cm^{-3}), in 4H-SiC epilayers is successfully achieved using DCS precursor.

2. Breakthrough in eliminating Si droplet and suppressing particles by using fluorinated silane

Silicon tetrafluoride (SiF_4) gas precursor with a significantly high Si-F bond strength is utilized to eliminate Si gas phase nucleation and Si parasitic deposition during silicon carbide (SiC) epitaxial growth, otherwise unachievable in similar growth conditions using conventional silane (SiH_4) and dichlorosilane ($SiCl_2H_2$/DCS) precursors. The significant higher Si-F bond strength (565 kJ/mol) in SiF_4 prevents early gas decomposition, essential for high temperature SiC CVD, and yet enables growth of high quality epitaxy in an improved particulate-suppressed growth condition. High quality, thick 4H-SiC epilayers >100μm have been demonstrated using SiF_4 with excellent surface morphology, polytype uniformity, crystallinity and low defect density.

As a novel Si precursor possessing high Si-F bond energy, TFS presents exceptional ability in the suppression of parasitic deposition that cannot be avoided in CVD growth using silane and chlorinated Si precursors. In SiC epigrowth using TFS, Si-droplet formation in the gas phase (i.e., gas-phase nucleation) is completely eliminated even at high TFS flow rates. TFS provides a clean environment for low cost and repeatable epigrowth. Excellent control of the

uniformities of morphology and doping concentration will make TFS especially suitable for large area (e.g., 6 inches) and multi-wafer (e.g., in planetary CVD reactor) CVD growth to achieve SiC devices with excellent performance uniformity. In terms of epilayer quality including morphology, roughness, crystallinity, polytype inclusion etc., epigrowth using TFS is found to be superior to the growth using DCS or silane precursors.

3. Doping Control and Crystal Quality

Excellent doping control, from highly n-type doped (up to 1e18cm^{-3}) to semi-insulating and to low p type (~1e15cm^{-3}), in 4H-SiC epilayers is successfully achieved using DCS precursor. The BPD and IGSF densities are as low as 0~5.6cm^{-2} when the growth is performed at C/Si ratio 1.1~1.8. For C/Si: 1.3–2.6, the epilayers are almost free of the inverted pyrimids and triangular defects. The epilayer RMS surface roughness is 1~2nm for C/Si>1.3. High quality and N doped epilayers are favorable to be fabricated at C/Si ratio=1.3~1.8 with addition of sufficient amount of N_2. Addition of N_2 does not show noticeable effects on defect generation, but may slightly (~10%) degrade the surface morphology.

4. On-axis 4H-SiC Epitaxial Growth

A reliable method to control polytype uniformity in nominally on-axis epigrowth at high C/Si ratio conditions was demostrated. The grown epilayers are of high quality, free of surface morphological defects except for some island formations of 3C-SiC. Epilayers with thickness ranging from low (5um/hr) to medium (~14 um/hr) is achieved which can be extensively used in making MOSFET or MESFET devices. High growth rates > 20 um/hr can be achieved by increasing the duration of growth, suitable for high-voltage devices.

5. Comparative study of Halogenated Precursors

From the comparative study of different precursors, it was observed that TFS is a superior precursor to DCS in several aspects such as reducing the parasitic deposition and Si gas phase nucleation; it has the ability to produce good surface morphology epilayers with an order of magnitude lower doping concentration than DCS. Higher growth rates with non-saturating behavior for TFS at high flow rates and high C/Si ratio growth capability proved to be an easy and effective way to reduce the BPD density on the grown epilayers. This makes TFS a potential and efficient Si precursor for growing device quality SiC epilayers.

6 Reduction/elimination of basal plane dislocations (BPDs) in epitaxial growth on 4° off-axis 4H-SiC

Epilayers with ~0 BPD density was achieved by a two-step epi-growth process by growing first a buffer epilayer of few micrometers thick with n-type doping ~1E16 cm^{-3} followed by etching the epilayer with MgO-KOH-NaOH mixture and again growing a second buffer epilayer of doping concentration ~ 1E 16 cm^{-3} above the etched epi-surface using DCS precursor.

7. *Schottky diodes fabricated on epilayers grown using TFS precursor*

Ni/4H-SiC Schottky diodes are fabricated on DCS-grown and TFS-grown epilayers. Near-ideal (ideality factor < 1.1), high barrier (barrier height > 1.6eV) Schottky behavior is obtained by post-deposition rapid thermal annealing of the contacts at 650°C in Ar environment. The tightest distribution of Schottky parameters is reported for Ni/SiC Schottky system fabricated on TFS-grown epilayer. The results were reproduced on wafers with doping levels varying from 10^{14}–10^{16} cm^{-3}, demonstrating the robustness and consistency of the process.

VII. Suggested future work

- Optimization of the reactor geometry (temperature gradient, pressure, etc.) can further reduce the parasitic deposition, especially in TFS-growth.
- Thick epitaxy on-axis 4H-SiC Growth at High Growth Rates
- A process to produce BPD-free epilayers in a single step.
- Close collaboration with industry to enable technology transfer and commercialization.

VIII. References

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